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An investigation of H-atom positions in sulfuric acid crystal structures

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Hydrogen conformations in crystalline $H_2SO_4{\cdot}8H_2O$ and $H_2SO_4{\cdot}6.5H_2O$ have been studied using a system developed by Hirsch [(2003), *Z. Anorg. Allg. Chem.* **629**, 666–672]. New H-atom coordinates, as estimated from DFT calculations, are given for these structures.

1. Introduction

H-atom positions in crystal structures are often very difficult to locate because the ability of H atoms to scatter X-rays is weak. Methods using neutron diffraction are more reliable when it comes to estimating H-atom coordinates, but such techniques have not been used to investigate the structures presented in this paper. However, it is possible to find H-atom positions theoretically. In the present paper, a method proposed by Hirsch (2003) is used to consider all possible H-atom positions in sulfuric acid–water mixtures that have a water content higher than 80 mol%.

Mootz & Merschenz-Quack (1987) estimated structural coordinates of $H_2SO_4{\cdot}8H_2O$ (Fig. 1) and $H_2SO_4{\cdot}6.5H_2O$ (Fig. 2) using X-ray diffraction experiments (ICSD COL numbers 63156 and 63155). All coordinates were refined, and the corresponding displacement parameters were given. The refinement is not as precise for the H atoms, which indicates that these coordinates are uncertain. It is also noteworthy that H_2SO_4 is fully deprotonated in the model. This model is surprising because the pH of the system investigated is approximately -0.7, thus indicating that approximately one ion in 500 is an SO_4^{2-} ion. It seems highly unlikely that the solution changes drastically at the freezing point, which probably means that many ions are still in the HSO_4^- form at the pH investigated by Mootz & Merschenz-Quack (1987).

2. Methods

According to the phase diagram of the solution studied in this paper (Fig. 3), the system is a mixture of the components $H_2SO_4{\cdot}6.5H_2O$, $H_2SO_4{\cdot}8H_2O$ and ice. When the system is diluted to $\sim 1.3 \times 10^{-4}$ mol% sulfuric acid (pH 2) and lower, there are more SO_4^{2-} than HSO_4^- ions. In this paper the two H_2SO_4 structures are investigated at pH values both less than and above 2.0.[1]

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA5005). Services for accessing these data are described at the back of the journal.

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2.1. $H_2SO_4{\cdot}8H_2O$

For the $H_2SO_4{\cdot}8H_2O$ structure it is impossible to use the space group proposed by Mootz & Merschenz-Quack (1987), because the symmetry elements only allow strained structures in which there are two H atoms intermediate between O atoms. We might argue that these positions are half populated or that they are under the influence of thermal motion and therefore jump between possible positions. This latter mechanism probably occurs in the temperature range studied by Mootz & Merschenz-Quack (1987), but there is certainly a preferred structure when the temperature is lowered even further. In the following arguments, all possible H-atom positions of the structures have been considered, but only those showing the lowest energies from the DFT calculations are presented.

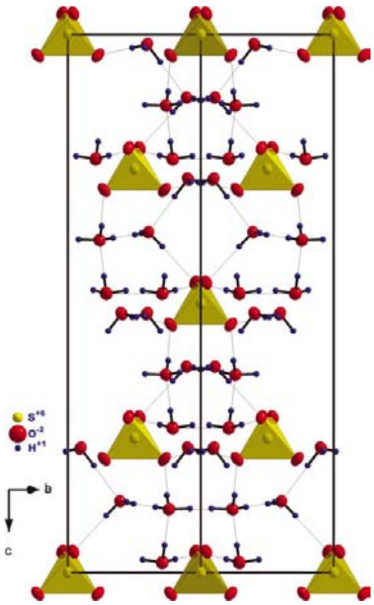

Figure 1
The unit cell of $H_2SO_4{\cdot}8H_2O$, as given by Mootz & Merschenz-Quack (1987).

Hirsch (2003) recommended lowering the symmetry of the structure when the previously given space group is too restrictive and then using combinatorial arguments to obtain all possible H-atom positions in the structure. Theoretical computations can then be used to single out the structure with the lowest energy.

The symmetry was lowered from $I\bar{4}2d$ (space group No. 122) to $C1c1$ (space group No. 9), using the computer program *JANA*2000 (Petricek & Dusek, 2000). In the new space group, H-atom positions are unique. All H-atom positions were generated by the scheme proposed by Hirsch (2003), and the criteria for positioning H atoms were as follows:

(i) An H atom was placed 0.97 Å from every O atom for which the O–O distance was less than 2.82 Å, but no H-atom positioning was allowed when both O atoms belonged to the same sulfuric acid molecule.

(ii) Only one H—O covalent bond per sulfuric acid ion was allowed, because only HSO_4^- and SO_4^{2-} ions exist at the pH of interest.

(iii) According to the stoichiometry of the system, there should be 18 H atoms for each S atom.

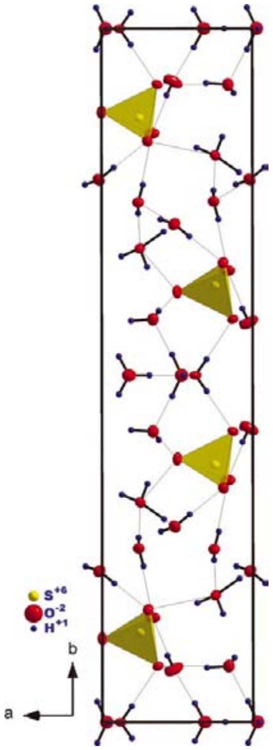

Figure 2
The unit cell of $H_2SO_4{\cdot}6.5H_2O$, as given by Mootz & Merschenz-Quack (1987).

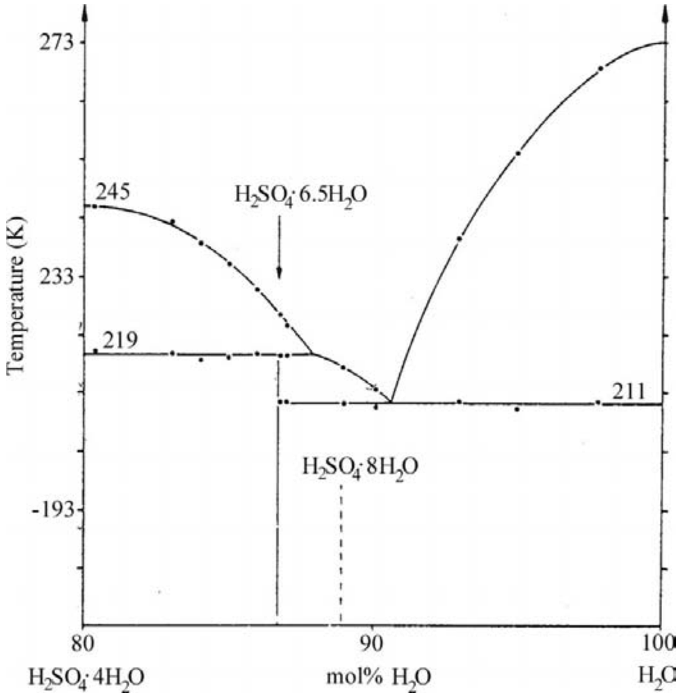

Figure 3
Phase diagram of water and H_2SO_4 (taken from Mootz & Merschenz-Quack, 1987).

Table 1
Distances and angles for $H_2SO_4{\cdot}8H_2O$ when only SO_4^{2-} ions are present.

Unit-cell parameters: $a = b = 10.560$ (4), $c = 11.952$ (11) Å, $\beta = 116.22°$. Symmetry: *C*1*c*1.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*a*—H2*aB*···O1*d*	1.00	1.74	2.735 (1)	174
O2*b*—H2*bB*···O2*c*	1.00	1.77	2.765 (1)	178
O2*d*—H2*dB*···O2*b*	1.00	1.76	2.762 (2)	177
O3*c*—H3*aA*···O3*a*	1.22	1.23	2.447 (2)	179
O3*a*—H3*aC*···O2*a*	1.01	1.65	2.654 (3)	173
O3*b*—H3*bB*···O1*b*	1.01	1.65	2.654 (2)	176
O3*b*—H3*bA*···O2*b*	1.01	1.65	2.654 (2)	173
O3*d*—H3*bC*···O3*b*	1.22	1.23	2.447 (2)	180
O2*a*—H2*aA*···O2*d*$^{\rm i}$	1.00	1.77	2.765 (1)	178
O3*d*—H3*dB*···O2*d*$^{\rm i}$	1.01	1.64	2.654 (2)	174
O3*c*—H3*cA*···O1*c*$^{\rm ii}$	1.01	1.65	2.654 (2)	176
O2*b*—H2*bA*···O1*c*$^{\rm ii}$	0.99	1.74	2.735 (2)	175
O2*c*—H2*cA*···O2*a*$^{\rm iii}$	1.00	1.76	2.762 (1)	177
O3*d*—H3*dA*···O1*d*$^{\rm iv}$	1.01	1.65	2.654 (2)	176
O2*c*—H2*cB*···O1*b*$^{\rm iv}$	1.00	1.74	2.735 (3)	176
O2*d*—H2*dA*···O1*a*$^{\rm v}$	1.00	1.74	2.735 (2)	176
O3*a*—H3*aB*···O1*a*$^{\rm vi}$	1.01	1.65	2.654 (2)	176
O3*c*—H3*cB*···O2*c*$^{\rm vii}$	1.01	1.64	2.654 (2)	173

Symmetry codes: (i) $x+\frac{1}{2}, y-\frac{1}{2}, z$; (ii) $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$; (iii) $x, y+1, z$; (iv) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (v) $x, 1-y, z+\frac{1}{2}$; (vi) $x, -y, z+\frac{1}{2}$; (vii) $x-\frac{1}{2}, y-\frac{1}{2}, z$.

Table 2
Distances and angles for $H_2SO_4{\cdot}8H_2O$ when only HSO_4^- ions are present.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*a*—H2*aB*···O1*d*	0.99	1.75	2.735 (1)	173
O2*b*—H2*bB*···O2*c*	1.00	1.77	2.765 (1)	177
O2*d*—H2*dB*···O2*b*	1.00	1.76	2.762 (2)	179
O3*c*—H3*cC*···O3*a*	1.02	1.43	2.447 (2)	180
O3*a*—H3*aC*···O2*a*	1.00	1.66	2.654 (3)	173
O3*b*—H3*bB*···O1*b*	0.98	1.68	2.654 (2)	170
O3*b*—H3*bA*···O2*b*	1.01	1.65	2.654 (2)	170
O3*d*—H3*dC*···O3*b*	1.13	1.32	2.447 (2)	179
O1*b*—H1*bA*···O2*c*$^{\rm i}$	1.10	1.64	2.735 (3)	175
O3*d*—H3*dB*···O2*d*$^{\rm ii}$	1.02	1.64	2.654 (2)	173
O2*a*—H2*aA*···O2*d*$^{\rm ii}$	0.99	1.77	2.765 (1)	176
O3*c*—H3*cA*···O1*c*$^{\rm iii}$	0.98	1.68	2.654 (2)	176
O2*b*—H2*bA*···O1*c*$^{\rm iii}$	0.99	1.75	2.735 (2)	174
O2*c*—H2*cA*···O2*a*$^{\rm iv}$	1.00	1.76	2.762 (1)	179
O3*d*—H3*dA*···O1*d*$^{\rm v}$	1.01	1.65	2.654 (2)	175
O2*c*—H2*cC*···O3*c*$^{\rm v}$	1.04	1.62	2.654 (2)	174
O2*d*—H2*dA*···O1*a*$^{\rm vi}$	0.99	1.75	2.735 (2)	175
O3*a*—H3*aB*···O1*a*$^{\rm vii}$	0.98	1.68	2.654 (2)	172

Symmetry codes: (i) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (ii) $x+\frac{1}{2}, y-\frac{1}{2}, z$; (iii) $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$; (iv) $x, y+1, z$; (v) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (vi) $x, 1-y, z+\frac{1}{2}$; (vii) $x, -y, z+\frac{1}{2}$.

It was extremely difficult to find all H-atom sites by inspection of the structure, and therefore a PERL program was constructed to discard the impossible structures; 191 structures were retained. Some of these structures are probably symmetry related, but no attempt to single out the symmetry-related structures was made. Of these 191 structures, 117 contain sulfuric acid ions in the HSO_4^- form, while the remaining 74 contain the SO_4^{2-} form.

Energy minimization was carried out on all these structures, using the classical potential model *COMPASS* (Sun, 1998). Over 40 of the structures that showed low energies, and five that showed higher energies, were evaluated again by energy minimizations using the DFT program *CASTEP*[2] (Milman *et al.*, 2000), and the structures that showed the lowest energy by the *CASTEP* method are those proposed in this paper. The *COMPASS* model shows some discrepancies with the *CASTEP* method, but the general trend is conclusive. It is noteworthy that the *CASTEP* method rearranges the H atoms to one preferred structure in many cases. The energy difference between the structure with the lowest energy and that with the highest was 83 kJ mol^{-1}, which is an indication that the hydrogen-bonding conformational energy is important to the overall energy of the system. According to these calculations, the structure in Fig. 4 (distances and angles are given in Table 1) is predominantly present when the pH of the system is greater than 2.0. Comparing this structure with Fig. 1, it is clear that two of the half-populated H-atom atom sites have been replaced by $H_5O_2^+$ ions and in the new structure the water molecule, which is represented as a half-populated H_3O^+ ion in Fig. 1, has adopted a preferred orientation. The existence of $H_5O_2^+$ ions is mentioned by Mootz & Merschenz-Quack (1987), but the H-atom positions are given as if there were two H atoms (half populated) connected to two H_3O^+ ions. Typical O—H—O distances for $H_5O_2^+$ ions lie in the range 2.4–2.5 Å (Attig & Williams, 1976; Selenius & Lundgren, 1980; Minkwitz & Hirsch, 1999), which agrees with the distance of 2.45 Å found in the present study. According to the same authors, typical O—H distances in such clusters are 1.08–1.22 Å. In the present study, the O—H distances are 1.22 and 1.23 Å, *i.e.* they are slightly longer but agree quite well with previous results.

When the pH is lower than 2.0, the structure in Fig. 5 and Table 2 should dominate according to pH calculations. However, DFT calculations show that the structure in Fig. 1 should still be predominant. On comparison of Fig. 5 with Fig. 1, it is evident that one of the O—O bonds that involved an $H_5O_2^+$ ion in the previous calculation now has an H_3O^+ ion in that position. The H-atom that still forms a contact with the

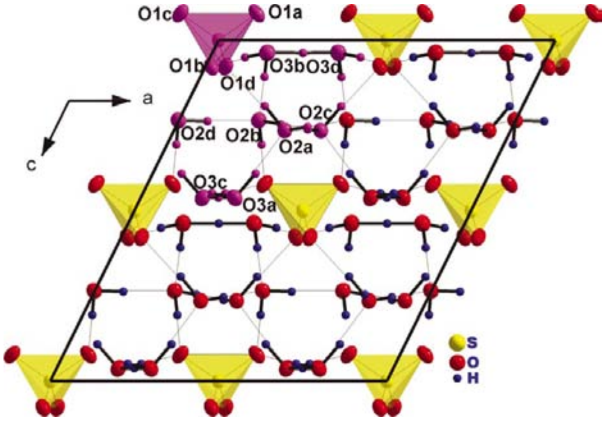

Figure 4
The calculated unit cell of $H_2SO_4{\cdot}8H_2O$ when only SO_4^{2-} ions are present. Note the $H_5O_2^+$ clusters that are predicted by the DFT calculations. Purple atoms indicate the asymmetric unit.

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[2] Accelrys Inc., San Diego, 2001, *CASTEP* User's Guide. http://www.tcm.phy.cam.ac.uk/castep/. Program developed by the TCM group, Cavendish Laboratory, University of Cambridge, UK.

Table 3
Distances and angles for $H_2SO_4 \cdot 6.5H_2O$ when only SO_4^{2-} ions are present.

Unit-cell parameters: a = 6.8182 (10), b = 26.876 (5), c = 5.9360 (10) Å, β = 121.4202°. Symmetry: $I1m1$ (No. 8).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5b···O7	1.01	1.63	2.634 (2)	176
O6—H6b···O4	0.98	1.80	2.755 (1)	165
O7—H7b···O2	0.98	1.79	2.763 (2)	173
O8—H8b···O9	1.03	1.43	2.465 (2)	178
O9—H9c···O4	0.98	1.79	2.767 (2)	172
O10—H10a···O1	0.99	1.75	2.734 (2)	178
O11—H11b···O10	1.00	1.66	2.653 (3)	173
O12—H12c···O1	0.98	1.78	2.757 (2)	175
O8—H8a···O10^{i}	1.00	1.66	2.654 (2)	178
O12—H12b···O3^{i}	0.98	1.74	2.719 (2)	172
O5—H5a···O2^{i}	1.00	1.61	2.610 (1)	174
O5—H5c···O6^{ii}	1.07	1.37	2.449 (3)	180
O6—H6a···O7^{iii}	0.99	1.72	2.705 (2)	173
O7—H7a···O3^{iv}	0.98	1.81	2.757 (2)	162
O9—H9a···O1^{v}	0.97	1.85	2.808 (3)	170
O11—H11a···O12^{vi}	1.04	1.45	2.485 (2)	175

Symmetry codes: (i) $x+1, y, z+1$; (ii) $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$; (iv) $x+1, y, z$; (v) $x, y, z+1$; (vi) $x-1, y, z$.

Table 4
Distances and angles for $H_2SO_4 \cdot 6.5H_2O$ when only HSO_4^- ions are present.

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2a···O7	1.07	1.69	2.763 (2)	174
O6—H6b···O4	0.97	1.84	2.755 (1)	157
O7—H7c···O5	1.01	1.62	2.634 (2)	178
O8—H8b···O9	1.03	1.43	2.465 (2)	178
O9—H9c···O4	0.98	1.80	2.767 (2)	172
O10—H10a···O1	0.98	1.75	2.734 (2)	178
O11—H11b···O10	0.99	1.67	2.653 (3)	173
O12—H12c···O1	0.98	1.79	2.757 (2)	175
O8—H8a···O10^{i}	1.00	1.66	2.654 (2)	179
O12—H12b···O3^{i}	0.98	1.75	2.719 (2)	169
O5—H5a···O2^{i}	0.95	1.68	2.610 (1)	166
O5—H5c···O6^{ii}	0.99	1.46	2.449 (3)	176
O6—H6a···O7^{iii}	0.98	1.73	2.705 (2)	174
O7—H7a···O3^{iv}	0.97	1.83	2.757 (2)	159
O9—H9a···O1^{v}	0.97	1.85	2.808 (3)	170
O11—H11a···O12^{vi}	1.04	1.45	2.485 (2)	174

Symmetry codes: (i) $x+1, y, z+1$; (ii) $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$; (iv) $x+1, y, z$; (v) $x, y, z+1$; (vi) $x-1, y, z$.

sulfuric acid ion has a large S—O—H angle (122.6°). This angle has been estimated for gaseous ions by supersonic jet experiments (Fiacco *et al.*, 2002), which showed that the angle should be ~107–110°. Another computational study, also for gaseous sulfuric acid (Johnson & Panas, 2002), showed that this angle should be ~105–109°. The reason for this discrepancy is probably that the hydrosulfuric acid ions must compensate for the crystal structure hydrogen-bonding network in which they are involved.

2.2. $H_2SO_4 \cdot 6.5H_2O$

The $H_2SO_4 \cdot 6.5H_2O$ structure was handled in exactly the same way as the $H_2SO_4 \cdot 8H_2O$ structure, but for $H_2SO_4 \cdot 6.5H_2O$ it is unnecessary to change the space group to make the hydrogen-bonding network plausible. However, the space group given by Mootz & Merschenz-Quack (1987) does not comply with the work of Mighell (2003) on cell choice, and therefore the space group was changed from $C1m1$ to $I1m1$. 34 possible structures were identified, of which 12 contain only SO_4^{2-} ions. As in the previous case, no attempt was made to identify symmetry-related structures. All of the structures were evaluated with *CASTEP*. According to pH calculations, the structure tabulated in Table 3 (Fig. 6) is the predominant structure when the pH is greater than 2.0. This structure is not remarkably different from that reported by Mootz & Merschenz-Quack (1987), but one hydroxonium H atom is definitely positioned differently.

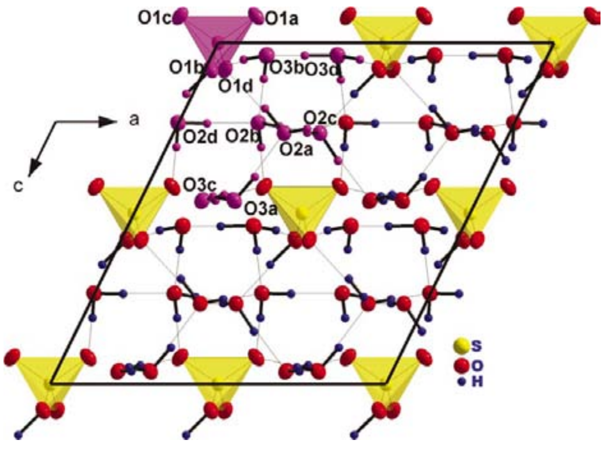

Figure 5
The calculated unit cell of $H_2SO_4 \cdot 8H_2O$ when only HSO_4^- ions are present. Purple atoms indicate the asymmetric unit.

For a pH below 2.0, the structure tabulated in Table 4 (Fig. 7) is the most stable according to pH calculations, but as in the previous case, the structure with only SO_4^{2-} ions is the most stable according to DFT calculations.

In this structure, the S—O—H angle is again large (118.8°).

2.3. Energy minimizations

DFT energy minimizations with the quantum mechanical package *CASTEP* were carried out to determine which of the calculated structures has the lowest energy. All minimizations assumed no symmetry whatsoever for the structures, that is, space group $P1$. Reorientation of atoms other than H atoms was prohibited. For the exchange correlation energies of the electrons, the GGA theory (Perdew, 1986; Becke, 1988) was assumed. The structures investigated here might be ion conductors but are unlikely to be electronically conducting, and therefore only the Γ point is needed. This k point was generated by the Monkhorst–Pack generation scheme (Monkhorst & Pack, 1976). Ultrasoft pseudopotentials, a coarse basis set of PW-91 and the density-mixing scheme proposed by Pulay (1980, 1982) were used. When a first estimation of the H-atom coordinates had been determined, the basis set was set to fine. The criteria for convergence were that the r.m.s. of the H-atom displacement should be less than 0.001 Å, the r.m.s. dispersion of the force on each atom should

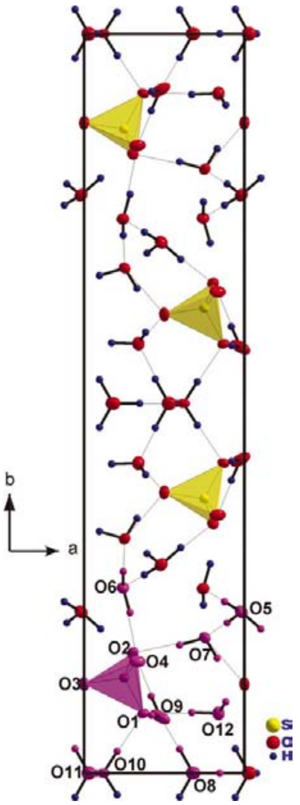

Figure 6
The calculated unit cell of $H_2SO_4{\cdot}6.5H_2O$ when only SO_4^{2-} ions are present. Purple atoms indicate the asymmetric unit.

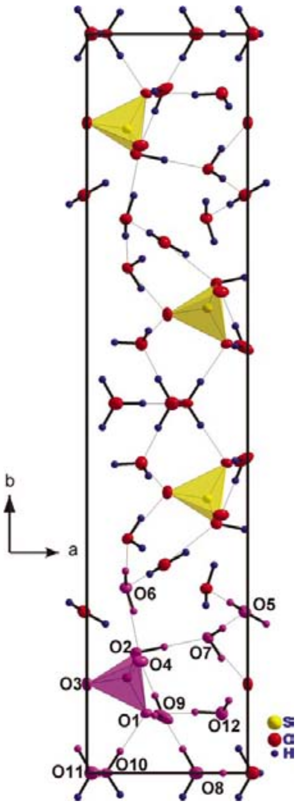

Figure 7
The calculated unit cell of $H_2SO_4{\cdot}6.5H_2O$ when only HSO_4^- ions are present. Purple atoms indicate the asymmetric unit.

be less than 0.05 eV Å^{-1} and the energy change per atom should be less than 0.2×10^{-5} eV.

3. Conclusions and discussion

According to the results presented here, two sulfuric acid structures have H-atom positions that differ slightly from those previously determined by X-ray diffraction experiments. The new information is based solely on theoretical arguments, but the evidence strongly supports the validity of the new coordinates. One interesting point is the $H_5O_2^+$ ions that are formed in the structure detailed in Table 1 and Fig. 4. The pH of the system studied by Mootz & Merschenz-Quack (1987) should be approximately −0.7, which, according to our calculations, strongly suggests the formation of the system in Table 2 and Fig. 5. However, the X-ray diffraction studies report a short O—O distance [2.45 Å], which indicates that there is a high probability that $H_5O_2^+$ ions will form. It is therefore possible that when the solution goes from the liquid to the solid state, a sudden change might occur as H atoms disconnect from the sulfuric acid ions and engage in new covalent bonding in the hydrogen-bonding water network.

It is also remarkable that the $H_5O_2^+$ ion is not formed in the $H_2SO_4{\cdot}6.5H_2O$ case, because the O5—O6 and O8—O9 distances are quite short (2.45 and 2.47 Å, respectively).

As a last remark, if future neutron diffraction experiments confirm the validity of the structures proposed here, this scheme might become a standard tool for estimating H-atom positions in crystal structures.

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